A new class of double alkyl-substituted, liquid crystalline imidazolium ionic liquids—a unique combination of structural features, viscosity effects, and thermal properties

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A new class of double alkyl-substituted, liquid crystalline imidazolium ionic liquids—a unique combination of structural features, viscosity effects, and thermal properties†

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1,3-Didodecylimidazolium salts have been prepared as first representatives of a new class of ionic liquid crystals (ILCs), showing thermotropic liquid crystalline behaviour in an extended temperature range below 70 °C. Remarkably strong non-Newtonian viscosity behaviour was found for the liquid-crystalline state of these ILCs.

Ionic liquids have attracted substantial interest in recent years. Their often unique property profile, such as extremely low vapour pressures, wide liquidus ranges, considerable electric conductivities, wide electrochemical windows and excellent tribologic properties have shown to be highly attractive for a large number of applications. A class of ionic liquid materials that promises great additional potential is ionic liquid crystals (ILCs). ILCs have been shown to exhibit exciting properties based on the combination of the anisotropic nature of their state of matter and their ionic liquid features. For example, ILCs are characterized by ionic conductivity together with uncommon ordering of the liquid-crystalline states (tetragonal smectic and nematic columnar phases).

Nowadays, 1-alkyl-3-methyl-imidazolium ions are by far the most popular cations for both, ILs and ILCs. For imidazolium salts with alkyl groups containing 12 or more carbon atoms, the formation of lamellar mesophases has been reported. Apart from ILCs based on imidazolium, quite a number of different head groups, such as ammonium and phosphonium but also more elaborate groups like vinamidinium, have been used in the past. Interestingly, both in IL and ILCs research the imidazolium head group is the most prominent one; probably because of its advantageous structural and electronic features and its easy derivatization.

In contrast to manifold optical applications, little attention has been paid to using other unusual properties that ILCs may offer.

We now report a new class of ILCs, for which the interplay of structural features, optical properties, and mechanical properties is documented and discussed. Our report concerns 1,3-didodecylimidazolium tetrafluoroborate, [C12C12IM][BF4] (1) and the corresponding perchlorate salt [C12C12IM][ClO4] (2), for which X-ray structural data, thermal range of liquid crystalline behaviour, and viscosity data are reported.

The new materials were synthesized by alkylation of 1,3-didodecylimidazole with dodecylchloride followed by ion exchange with Na[BF4] and Na[ClO4], respectively. The crystal packing diagrams of tetrafluoroborate 1 and perchlorate salt 2 are shown in Fig. 1 and 2.

In both structures, the cations are characterized by a rod shape with the two alkyl chains being stretched outward along the imidazolium core plane. The two alkyl chains are arranged in an all-staggered fashion. In this respect, 1 and 2 resemble other rod-shaped systems like [C14-C14(2-OH)-IM][Br] or the AgX2-bridged (X = Br, Cl) silver metalted coordination complexes [Ag(C14-IMY-C14)][AgBr2] and [Ag(C14-IMY-C14)][AgCl2] (IMY: imidazol-2-ylidene). While the imidazolide units in these systems as well as in [C12C12IM][BF4] (1) exhibit basically a parallel arrangement of their alkyl chains, in [C12C12IM][ClO4] (2) a significant deviation from linearity is observed. In order to estimate the degree of this deviation, the angle between the two alkyl arms (defined as the angle between the imidazolium ring centroid and the terminal dodecyl group C atoms) has been calculated. While this angle is typically close to 180° and, for instance, up to 172° in tetrafluoroborate salt 1, the angle is reduced to 152° in the molecular structure of the cation of perchlorate 2 (see Fig. 2). As is observed for the crystal packing of other rod-shaped systems, the imidazolium moieties together with the tetrafluoroborate (1) or perchlorate (2) anions form hydrophilic stacks, while the hydrophobic dodecyl chains

Fig. 1 Packing diagram of [C12C12IM][BF4] (1); view along crystallographic a axis highlighting the zig-zag arrangement within the bc plane.
show strong interdigitation. In 1 and 2, the interdigitation is observed within both the crystallographic ac and bc planes. Due to the 152° bent angle between the two alkyl arms the packing of 2 is characterized by a pronounced zig-zag arrangement of molecules within the bc plane (see Fig. 2).

In the following we were interested to study the temperature range in which these ILCs exhibit liquid crystalline behaviour. Fig. 3 shows the DSC of 2, the corresponding DSC of 1 is shown in the Supporting Information.

It was found that the new ILCs exhibit transitions to the liquid crystalline state at surprisingly low temperatures. Cooling the liquid system from the isotropic liquid state in the DSC with 5 K min⁻¹, 1 showed a transition to the liquid-crystalline state at 67 °C and crystallized at 34 °C (onset). In contrast, 2 turned liquid crystalline at 64 °C and crystallised at 28 °C. In addition the DSC trace of 1 shows two more thermal events below room temperature, which can be attributed to solid-solid phase transitions. Subsequent heating shows all thermal processes to be reversible. However, as typical for ILs, a pronounced temperature shift is observed for the crystallization process. In both cases, the transition to the liquid crystalline state could be followed by polarizing optical microscopy. The observed focal conical textures point to smectic phases (see Supporting Information). This type of ordering in the liquid state is already suggested by the solid state structures of both compounds.

To the best of our knowledge, no ionic liquids are reported to date that show a drastic non-Newtonian viscosity behaviour, which means that the viscosity of known ionic liquids is independent of the shear rate applied to the sample. As an ever increasing number of ionic liquid applications are discussed, in which viscosity is a key property (e.g. for the use of ionic liquids as lubricants) we were interested whether the known non-Newtonian viscosity behaviour of non-ionic liquid crystals does also apply to our new class of ionic liquids and to which extent these materials exhibit viscosity changes with shear rate. Fig. 4 and 5 display the respective viscosity shear rate diagrams for 1 and 2.

Remarkably, by going from the liquid phase to the liquid crystalline phase, a sudden and very strong change in the viscosity versus shear rate behaviour is found for both ILCs. The viscosity of 1, for example, abruptly increases from 136 mPa s at 80 °C to 1720 mPa s at 70 °C (at a shear rate of 40 s⁻¹). For a better comparison of the effect of a change of 10 °C in the liquid range, the viscosity at 90 °C is also given. As expected, perfect Newtonian behaviour is found with a viscosity of 89 mPa s being determined.

In conclusion, in this work a new class of imidazolium based ILCs is presented, namely bis(dodecyl) substituted [BF₄]⁻ and [ClO₄]⁻ imidazolium salts. These salts are solids at room temperature and display extended ionic channels and mutually interacting alkyl domains in their crystal structures. At remarkably low temperatures, the new materials show a transition into mesophases. For the latter we could show,
for the first time, a strongly non-Newtonian viscosity behaviour for ionic liquids that can be switched on and off by keeping the temperature above or below the phase transition temperature. This property combined with the well-known ionic liquid features, such as extremely low vapor pressure, electroconductivity, and excellent tribological properties, makes these materials of great potential as working fluids in mechanical applications or as functional materials with thermomorphic properties.

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